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NRL Memorandum Report 5210

## Possible Role of vibrationally excited Hydrogen in the Chemistry of the Earth's Upper Atmosphere

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The possible role of vibrationally excited $H_2^*$ ( $H_2^*$ ) on the budget of $H_2$ in the earth's mesosphere and lower thermosphere is considered and found to be negligible ( $\sim 2\%$ at 80 km). Our model includes production, chemical reactions, and quenching reactions of $H_2(v = 0-5)$ . We estimate that at 80 km, where $H_2$ production is maximized, the rate of the $H_2$ removing reaction $O(^3P) + H_2^* \rightarrow OH + H$ does not exceed $6.4 \times 10^{-12} \text{ cm molec}^{-1} \text{ sec}^{-1}$ for $v = 5$ , which is sufficiently slow that quenching removes most $H_2^*$ before it can react with $O(^3P)$ .		

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## POSSIBLE ROLE OF VIBRATIONALLY EXCITED HYDROGEN IN THE CHEMISTRY OF THE EARTH'S UPPER ATMOSPHERE

### I. Introduction

The chemistry of vibrationally excited molecules in the earth's atmosphere is a subject which has received substantial attention (Dalgarno, 1963; Cvetanovic, 1974; Taylor, 1974, Vlasov, 1976). Much of this attention has been due to the fact that emission from vibrationally excited molecules in the upper atmosphere is known to be responsible for major portions of the earth's airglow, most notably the Meinel bands of OH (Bates, 1982 and references therein). Infrared emission from vibrationally excited molecules in the thermosphere is also expected to play a major role in atmospheric cooling (Gordiets *et al.*, 1982).

There is little evidence that chemical reactions of vibrationally excited species play an important role in controlling the net photochemistry of the earth's upper atmosphere, however. By this, we mean that it is not expected that processes of the type



will be important while processes such as



are not (an asterisk is used here to represent vibrational excitation). Crutzen (1974) suggested one case where vibrational excitation could play a very important role. This case is the reaction



which is known to occur very slowly at low and moderate temperatures due to a large (~ 8.5 kcal/mole) activation energy. Because the  $H_2$  vibrational quantum is large (10.2 kcal/mole) and vibrational excitation of  $H_2$  is likely in  $H_2$  forming reactions, Crutzen suggested that reaction 2 could be sufficiently accelerated by vibrational excitation of  $H_2$  that it might become

one of the dominant loss processes for  $H_2$ . He showed that if one assumed a temperature independent rate constant of  $2.9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1}$  for the reaction



the predicted concentration of  $H_2$  at and above the 80 km level of the atmosphere decreased by nearly 50%.

This increased destruction of  $H_2$  by reaction (2b) led to a substantial increase in the mixing ratios of  $H_2O$  above 70 km calculated by Crutzen (1974). Odd hydrogen ( $HO_x$ ) formed as a result of  $H_2O$  photolysis is known to lead to ozone ( $O_3$ ) depletion by catalytic cycles, and such reductions are expected to be especially strong at higher altitudes (Prather, 1981). As the ability to measure  $O_3$  in the upper mesosphere and lower thermosphere is increasing, the uncertainty in the  $H_2O$  concentration of the magnitude indicated by Crutzen (1974) due to the possible role of  $H_2^*$  becomes unacceptably large. Thus, it is important that the role of reaction (2b) as a means of altering the upper atmospheric  $H_2$  and  $H_2O$  balance and, therefore, the  $O_3$  concentration be established.

Recent experimental work (Light, 1978) indicates that Crutzen seriously overestimated the effect of  $H_2$  vibrational excitation on the rate of reaction 2, and theoretical calculations (Schinke and Lester, 1979) suggest that more than two vibrational quanta of excitation are needed for the rate of reaction 2 to even begin to approach the value suggested by Crutzen.

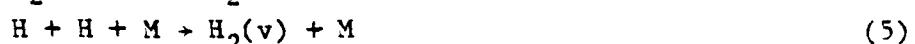
In this report we examine in some detail the aeronomy of vibrationally excited  $H_2$ , hereafter referred to as  $H_2^*$ , in the earth's upper atmosphere. We consider processes responsible for production and destruction of  $H_2^*$ , and attempt to make reasonable estimates for the vibrational state specific chemical reaction and vibrational quenching rates. Finally, we combine the expressions obtained with a knowledge of the photochemistry of  $H_2$  in the atmosphere (Hunten and Strobel, 1974; Liu and Donhue, 1974; Schmidt, 1974; Koshelev, 1976; Penner *et al.*, 1977) to conclude that consideration of  $H_2^*$  is not expected to appreciably alter the calculated upper atmospheric  $H_2$  densities.

## II. Chemical Model

In this section we will briefly review all chemical reactions which we expect to be important in the aeronomy of  $H_2^*$ ; we will defer estimation of state specific rate constants to Section III. We will consider processes responsible for production, loss by reaction, and loss by inelastic processes of  $H_2^*$ .

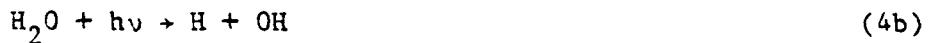
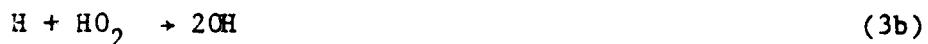
### A. Production of $H_2^*$

Crutzen (1974) suggested three processes which can reasonably be assumed to give rise to  $H_2^*$  in the earth's upper atmosphere:



Of these, the small concentrations of H in the earth's upper atmosphere and the slow rate for R5 combine to make it unimportant. Model calculations of Hunten and Strobel (1974) show that the fractional contribution of R5 to  $H_2$  production near its peak at 80 km must be not greater than 1 part in  $10^4$ . Thus, we will restrict our attention to the potentially important reactions R3 and R4a.

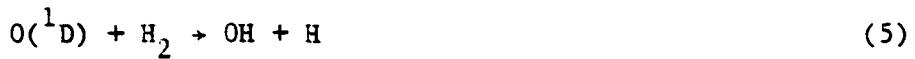
We note that R3a and R4a represent each only one possible product path for the respective reactions. Alternate (and frequently more prevalent paths) are



While the exact portion of reactions 3 and 4 resulting in  $H_2$  formation by pathways 3a and 4a, respectively, is not precisely determined (Hack et al. 1978; Sridharan et al. 1982; Stief et al., 1975; Slanger and Black, 1982); the results of our analysis do not depend strongly on the branching ratios R3a/R3 and R4a/R4 unless we have greatly underestimated them.

### B. Loss of $H_2^*$ by Chemical Reaction

Three  $H_2$  destruction reactions were considered by Crutzen (1974):

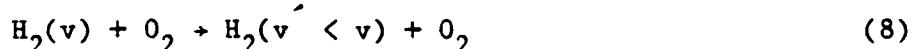
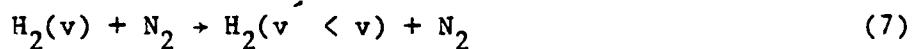


Of these, it is expected the R2 is the only one which will be important for  $H_2^*$ . Reaction 5 is known to occur rapidly ( $k_5 = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$  and no temperature dependence) with ground vibrational state  $H_2$  (JPL, 1982), so vibrational excitation is not expected to appreciably accelerate it. Supporting this expectation, quasi-classical trajectory calculations for R5 show only a 10% increase in reaction cross section on  $H_2$  vibrational excitation (Schinke and Lester, 1980). Since  $[O(^1D)] \ll [O(^3P)]$ , we may thus safely neglect the effect of R5 on  $H_2^*$ .

Reaction 6, which is known to have a substantial (4 kcal/mole) activation energy (JPL, 1982) could be expected to be appreciably accelerated by  $H_2$  vibrational excitation, especially at low temperatures. At room temperature, single quantum excitation of  $H_2$  is known to increase the rate of R6 by roughly a factor of 100 (Glass and Chaturvedi, 1981), corresponding to an approximate decrease in the activation energy from 4 to 2.5 kcal/mole (Truhlar and Isaacson, 1982). Even if multiple-quantum excitation of  $H_2$  sufficiently accelerates R6 that there is no effective activation barrier, the low concentration of OH in the mesosphere, as opposed to that of  $O(^3P)$ , (Prather, 1981) indicates that R2 should be much more important than R6, and we will thus consider R2 as the only reactive loss process for  $H_2^*$ .

### C. Loss of $H_2^*$ in Inelastic Collisions

We will need to consider three major non-reactive loss process for  $H_2^*$ :



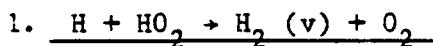


where we write here  $H_2^*$  as  $H_2(v)$  to reinforce the state-specificity of the quenching rates. Since there is no information on the rate of R8, we will assume that the rates for quenching of  $H_2(v)$  by  $N_2$  and  $O_2$  are identical. This is a reasonable assumption, given the similarities of  $N_2$  and  $O_2$  in terms of mass, vibrational frequencies, and Lennard-Jones potential parameters (Lambert, 1977).

The only measurement of the rate of R7 is for  $v=1$  at room temperature (Bott, 1976) and is, therefore, not directly applicable to the high excitation and low temperatures encountered in the upper atmosphere. We will attempt to make reasonable approximations for the  $v$  and  $T$  dependence of the rate of R7. There are no measurements of the rate of R9, and no results were presented for  $H_2$  vibrational deactivation in quasi-classical trajectory calculations on R2 (Schinke and Lester, 1979), so we will be forced to estimate the rate of R9.

### III. Estimation of State-Specific Reaction Rates and Branching Ratios

#### A. Production of $H_2^*$



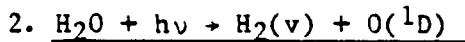
Reaction 3a is sufficiently exothermic (2.25 eV if the  $O_2$  is produced in its ground electronic state) that the  $v = 0-4$  vibrational levels of  $H_2$  are energetically accessible. If the  $O_2$  is produced in one of its low-lying electronically excited states ( $a_g^1 \Delta$ ,  $b_g^1 \Sigma^+$ ), less energy is available for  $H_2$  product internal excitation. Experiments indicate that the yield of electronically excited  $O_2$  in reaction 3a is quite small (Washida *et al.*, 1978) and we will assume, therefore, that reaction 3a proceeds only to ground electronic state products.

No information is available on the distribution of internal energy in the products of reaction 3a. Quasi-classical trajectory calculations on a related reaction

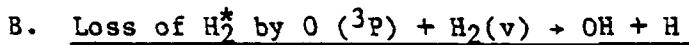


have been performed (Fanantos and Murrell, 1980). They showed that between 25% and 30% of the available product energy goes into  $H_2$  vibration in the temperature range 300-1000K, and that the  $H_2$  vibrational state distribution is

approximately Boltzmann. If we assume these conclusions carry over to reaction 3a, we estimate a product state distribution for  $v = 0, 1, 2, 3$ , and  $4$  respectively of  $0.35: 0.25: 0.18: 0.13: 0.09$ .



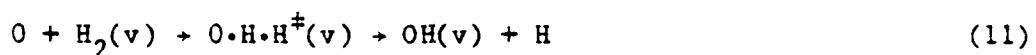
Nothing is known of the  $\text{H}_2$  vibrational state distribution in this process. Substantial vibrational excitation of  $\text{H}_2$  is energetically permitted; the endothermicity of the dissociation process is  $7.06\text{eV}$ , and a photon at  $1216 \text{\AA}$  (Ly- $\alpha$  , expected to be the most important vacuum ultraviolet wavelength) contains  $10.20\text{eV}$ , leaving  $3.14\text{eV}$  available for product excitation. Given that there is an appreciable change in the H-H distance on photodissociation, substantial vibrational excitation of the  $\text{H}_2$  product is a distinct possibility. If we estimate that  $20\%$  of this available energy goes into  $\text{H}_2$  and assume that the vibrational states are populated with a Boltzmann distribution, a product state distribution for  $v = 0, 1, 2, 3, 4$ , and  $v > 5$  of  $0.4: 0.2: 0.1: 0.08: 0.05: 0.06$  is expected. This distribution is reasonably close, especially at the high vibrational excitation end, to that which would be expected on a purely statistical basis (i.e. product states are populated proportionately to the density of states).



The available data, both experimental (Light, 1978) and theoretical (Schinke and Lester, 1979) indicate that  $\text{H}_2$  vibrational excitation leads to an enhancement in its rate by a factor much smaller than that assumed by Crutzen (1974). At room temperature Light (1978) measured a rate constant of  $1.0 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$  for R2b with  $v=1$ . No measurements of this reaction at the lower temperatures of the earth's mesosphere and lower thermosphere have been reported. Two quantum excitation of  $\text{H}_2$  has been calculated to lead to an additional factor of 100 enhancement over the rate for R2b( $v = 1$ ) at 300K (Schinke and Lester, 1979), which gives an approximate value of  $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$  for R2b ( $v = 2$ ) at 300K. In order for R2b to occur rapidly ( $k_{2b} > 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ ) we clearly require high vibrational excitation. As we showed earlier, population to  $v = 5$  is probable, so detailed consideration of these higher levels is appropriate.

A simple picture which permits one to make reasonable predictions for the effect of vibrational energy on chemical reactions involves a combination of transition state theory and the vibrationally adiabatic theory of chemical reactions (Kuppermann, 1979 and references therein). In this picture, one specifically accounts for the fact that large effective energy barriers to chemical reactions may persist even when the amount of vibrational excitation is very large (Kaye, 1982). This method has been applied to R2 ( $v = 0, 1$ ) and shown to give reasonable results (Lee et al., 1982b), and we use a simplified version of this model to make predictions for the temperature and quantum state dependence of R2b.

The crucial step in this method is the recognition that the position and energy of the transition states (represented by  $\ddagger$ ) of the chemical reaction



depend on the reagent vibrational quantum number  $v$ . The transition-state theory expression for the state-specific is

$$k_v(T) = K(T) \frac{kT}{h} \frac{f_{tr}^\ddagger}{f_{tr}^0 f_{tr}^{H_2}} \frac{(f_b)^2 v (f_{rot})_v^\ddagger}{(f_{rot})_v^{H_2}} \exp(-\Delta V_v^\ddagger / kT) \quad (12)$$

where  $f_{tr}$  is a translational partition function,  $f_{tr} = (2\pi mkT/h^2)^{3/2}$ ,  $f_b$  is the bending partition function not including zero-point energy,  $f_b = [1 - \exp(-hv_{b,v}/kT)]^{-1}$ , and  $f_{rot}$  is a rotational partition function.  $\Delta V_v^\ddagger$  is the  $v$ -dependent height of the vibrationally adiabatic barrier to chemical reaction which includes stretching and bending zero-point energies.  $K(T)$  is a dynamical correction factor which we will take to be unity for reasons described below. In usual applications of transition state theory there are also terms for reagent vibration and complex "symmetric-stretching" type modes but these are not considered here because our model restricts us to one vibrational state at a time; in any case both these modes are at a sufficiently high frequency that at mesospheric temperatures their

value is unity.

The position and energy of the vibrationally adiabatic barriers for R2 are determined by the method described by Lee et al. (1982) except that eigen-values were determined numerically (Truhlar 1972) rather than by a fit to a Morse oscillator, using the MOD POL-CI RMOS potential energy surface (Lee et al., 1982a). Transition state rotational partition functions were calculated using the geometries calculated for each transition state, under the rigid-rotor approximation.  $H_2$  rotational partition functions are independent of  $v$  in the harmonic oscillator approximation for  $H_2$ . Complex bending partition function were calculated using an assumed form [ $\nu_{b,v} = A \exp(-bs_v^2)$ ] for the dependence of the bending frequency on the distance  $s_v$  of the  $v^{\text{th}}$  transition state along the reaction coordinate from the saddle point. Since the MOD POL-CI RMOS surface (Lee et al., 1982a) is defined only for collinear configurations, we estimated  $b$  using the Johnson-Winter (JW) potential energy surface (Johnson and Winter, 1977).  $A$  was assumed to have the value of  $514 \text{ cm}^{-1}$  determined by Walch et al. (1980) for their  ${}^3A''$  surface. Bending frequencies were calculated using standard formulas for linear triatomic molecules (Johnston, 1966). Values of various quantities in Eq. 12 and parameters used to calculate these values in Eq. 12 are shown in Table 1.

We note that the MOD POL-CI RMOS surface does not have the correct asymptotic vibrational energy levels for  $H_2$ , but this is not expected to lead to appreciable errors except for  $v=0$  (where the barrier is assumed to be at the saddle point). The vibrationally adiabatic barriers are sufficiently far in the entrance channel (closer to  $0 + H_2$  than  $OH + H$ ) that the heights and positions of the barriers are probably correct; only their absolute energies are wrong, and they do not enter into these calculations. The dynamical correction factors  $K(T)$  are taken to be unity as a reasonable compromise between two competing effects. At low  $T$ , quantum mechanical tunneling tends to make  $K(T)$  large ( $>1$ ) while at high  $T$ , reaction probabilities are always  $<1$ , so  $K(T) < 1$  also. Thus we feel our choice for  $K(T)$  is a physically reasonable one. If anything, this may be a slight overestimate of  $K(T)$ , which means we are overestimating  $k_v(T)$  and thus overestimating the importance of R2b. More accurate determination of  $K(T)$  is possible (Bowman et al., 1981; Lee et al., 1982b) but becomes expensive because of the large internal excitation we must consider here.

Table 1

Values of Quantities Used in Estimating Rate Constants for  
the Reaction  $O + H_2(v) \rightarrow OH + H$

$v$	$v_v^\pm$ <sup>a</sup>	$V[H_2(v)]$ <sup>a</sup>	$(R_{OH}^\pm)$ <sup>b</sup>	$(R_{H_2}^\pm)$ <sup>b</sup> <sub>v</sub>	$I_v^\pm$ <sup>c</sup>	$v_{s,v}^\pm$ <sup>d</sup>	$v_{b,v}^\pm$ <sup>d</sup>	$\Delta V_v^\pm$ <sup>a</sup>	
0	-3.486	-3.872		2.33 1.74		3.22(-39)	1636	514	0.450
1	-3.190	-3.375		3.01 1.49		4.36(-39)	3750	488	0.246
2	-2.812	-2.913		3.39 1.46		5.22(-39)	4090	451	0.157
3	-2.429	-2.485		3.83 1.44		6.32(-39)	4210	389	0.104
4	-2.048	-2.091		4.05 1.43		6.93(-39)	4280	355	0.087
5	-1.703	-1.732		4.27 1.44		7.57(-39)	4280	319	0.069

a) Potentials are measured (in eV) with respect to a zero energy at three infinitely separated atoms.  $v_v^\pm$  = height at top of  $v^{\text{th}}$  vibrationally adiabatic barrier.

$V[H_2(v)]$  = energy of  $v^{\text{th}}$  vibrational level of  $H_2$

$\Delta V_v^\pm$  = vibrationally adiabatic barrier height

b)  $R_{xy}^\pm$  is xy internuclear distance (in bohr) at  $v^{\text{th}}$  transition state

c)  $I_v^\pm$  is moment of inertia (in  $\text{g cm}^2$ ) of  $v^{\text{th}}$  transition state.

Numbers in parentheses represent powers of ten by which the non-enclosed numbers should be multiplied.

d)  $v_{s,v}^\pm$ ,  $v_{b,v}^\pm$  are "symmetric stretch" and bending vibrational frequencies respectively (in  $\text{cm}^{-1}$ ) at  $v^{\text{th}}$  transition state

Using the data in Table 1 and eq. 12 we find an expression for the rate constant of

$$k_v(T) = a_v [1 - \exp(-b_v/T)]^{-2} T^{1/2} \exp(-c_v/T) \quad (13)$$

Values of the constants  $a_v$ ,  $b_v$ , and  $c_v$ , along with  $k_v$  at  $T=200$ ,  $300K$  are given in Table 2. The  $300K$  result for  $v = 1$  agrees quite well with the result of  $1(+0.9, 0.6) \times 10^{-14} \text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$  determined by Light (1978).

### C. Loss of $H_2^*$ in Inelastic Collisions

#### 1. $H_2(v) + N_2 \rightarrow H_2(v' < v) + N_2$

Due to the fact that the rate for this process is known only for  $v = 1$  at room temperature, we must theoretically extend these results to the lower temperatures and higher levels of excitation encountered in the upper atmosphere. Simple methods for estimating rates of vibrational-to-vibrational (V-V) and vibrational (V-T) energy transfer, such as SSH theory and its derivatives (Lambert 1977 and references therein) give unreasonable results for  $H_2$  and thus may not be used.

Some aspects generally seen in energy transfer collisions are expected be true for this process. Specifically, we expect all such deactivations to occur in single quantum transitions and the deactivation rate to be proportional to the level of  $H_2$  excitation:

$$k_{v,v-1} = v k_{1,0} \quad (14)$$

Rather than assuming the usual  $T$  dependence for deactivation rates (Lambert, 1977) in this system, we will assume that the  $k_{v,v-1}$  are  $T$  independent. Our motivation for this comes from noting that in order to ensure that transition probabilities obey microscopic reversibility, simple expressions for them must contain a term of the form  $\exp(\Delta E/2kT)$ .  $\Delta E$  is the energy being converted from vibration to translation and is positive for deactivation and negative for excitation. Combining this dependence with usual  $T$  dependence we see in the simple theories

$$P_{10} \propto \exp(-BT^{-1/3}) \exp(\Delta E/2kT) \quad (15)$$

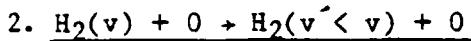
Table 2: State Specific Rates  $k_v(T)$  for the Reaction  $O + H_2(v) \rightarrow OH + H$

$v$	$a_v^{\ddagger}$	$b_v(^0K)$	$c_v(^0K)$	$k_v(200K)$	$k_v(300K)$
0	1.72(-9)		740	5220	5.85(-22)
1	2.32(-9)		703	2850	1.11(-16)
2	2.78(-9)		650	1820	2.35(-14)
3	3.37(-9)		556	1210	6.48(-13)
4	3.69(-9)		512	1010	1.96(-12)
5	4.04(-9)		460	800	6.43(-12)

\*Rate constants have units of  $cm^3molec^{-1}sec^{-1}$ . The numbers in parentheses represent the power of ten by which the non-enclosed number should be multiplied.

Clearly, at sufficiently low T,  $P_{10}$  will increase with T. Using reasonable values for the collection of parameters B and  $\Delta E$  we expect no enormous reduction in  $P_{10}$  from 300-200K (no more than a factor of three), and thus assume no T dependence for the deactivation rate. This assumption probably leads to a slight overestimate of the  $N_2$  quenching rate and thus a slight underestimation of  $H_2^*$  concentrations and hence of its role in atmospheric chemistry.

Since our neglect of the transmission coefficient in section B above probably led to an overestimate of the rate of R2b, we think these assumptions should more or less cancel each other out.



It is known that vibrational deactivation in potentially reactive collisions may be an extremely rapid process (Smith, 1976), and for this reason we must consider this process as a potential loss mechanism for  $H_2^*$ . In addition, it has been seen in collinear quantum mechanical scattering calculations in atom-diatom systems that multi-quantum transitions, may account for a substantial fraction of deactivation collisions (Kaye, 1982).

In order to assess the relative magnitude of this process and, in particular, the importance of multi-quantum transitions we have performed collinear quantum mechanical scattering calculations on this system using the MOD POL-CI RMOS surface (Lee *et al.*, 1982a). For simplicity, we will consider one n-quantum transition as n single-quantum transitions. We estimate the rate of deactivation by this process to be given by

$$k_{v,v-1}^{(9)}(T) = R_v(T) k_v^{(2)}(T) \quad (16)$$

where the superscript represents the reaction number;  $k_v^{(2)}$  is given by eq. 12 or alternatively by eq. 13 and Table 2, and  $R_v(T)$  is determined from the collinear quantum mechanical calculations by the expression

$$R_v(T) = \frac{\sum_{v=1}^{v-1} (v-v') k_{vv}^{(9)}(T)}{k_v^{(2)}(T)} \quad (17)$$

where the  $k$ 's in eq. 17 are the calculated collinear ones. Results of the calculations indicate nearly T independent values of  $R_v(T)$  of 0.4, 0.7, and

0.9 for  $v = 1, 2$ , and 3 respectively. We further assume values of 1.0 for  $v = 4$  and 5. The assumption that one may use the results of collinear calculations to make predictions about the real three-dimensional world has been made frequently in the past (Bowman *et al.*, 1981; Lee *et al.*, 1982b; Wassam and Lee, 1976; Wassam, 1980). and, while certainly not being exact, should give physically reasonable results.

#### IV. Aeronomy of $H_2^*$

To evaluate the possible importance of R2b in controlling the  $H_2^*$  concentration in the earth's upper atmosphere, we will consider a simple steady-state purely photochemical model (i.e. containing no transport) for the 80 km altitude region, at which  $H_2^*$  production is expected to be a maximum (Hunten and Strobel, 1974; Liu and Donahue, 1974). For convenience we adopt results from the former. Although numerous reaction rate constants and branching ratios have been assigned new values since that work was performed, the qualitative picture remains unchanged. We thus assume that the conclusions we draw about the role of  $H_2^*$  should also be valid in a model using more recent values for the many parameters necessary.

Concentrations of important species and reaction rates are taken from the appendix and Figures 2 and 3 of Hunten and Strobel (1974) and are shown in Table 3 here. Pertinent rate constants and reaction rates are shown for  $v = 0-5$  at 80 km in Table 4.

The assumption of steady for  $H_2^*$  implies the following expressions:

$$\begin{aligned} \frac{d[H_2(v)]}{dt} = 0 = & R_v^{(3a)} + R_v^{(4a)} - \{ (k_v^{(12)} + k_v^{(9)})[0] + \\ & k_v^{(7)}[N] + k^{(5)}[O(^1D)] \}[H_2(v)] \\ & + (k_{v+1}^{(7)}[M] + k_{v+1}^{(11)}[O])[H_2(v+1)] \end{aligned} \quad (18)$$

where we repeat that we are considering only single quantum deactivations and we neglect vibrational excitation. These equations may be rewritten in matrix form

$$Kx = -R \quad (19)$$

Table 3: Parameters of Importance to  $H_2^*$  Aeronomy

(Taken from appendix and Figures 2 and 3 of Hunten and Strobel, 1974)

$z(\text{km})$	$T(\text{K})$	$[M]$	$[O]$	$[O(^1\text{D})]$	$[H_2]$	$R^{(3a)}\text{b}$	$R^{(4a)}\text{b}$
50	271	2.14(16)	3.25(9)	3.05(2)	1.5(9)	1	0
60	243.3	6.47(15)	3.25(9)	1.3(2)	2(9)	2	0
70	216.6	1.70(15)	2.0(9)	4.8(1)	1.5(9)	6	25
80	186	3.76(14)	7.0(9)	3.5(1)	8(8)	80	100
90	183	6.39(13)	2.2(11)	1.5(2)	1.5(8)	0.05	6
100	193.5	9.74(12)	8.0(11)	6.0(2)	2(7)	0.001	0.1

\* Concentrations are in units of  $\text{cm}^{-3}$ , Reaction rates (R) are in units of  $\text{cm}^{-3}\text{sec}^{-1}$ . Numbers enclosed in parentheses are the powers of 10 by which the non-enclosed numbers should be multiplied.

Table 4: Data for Steady State Calculation at 80 km\*

$v$	$R_v^{(3a)}$	$R_v^{(4a)}$	$k_v^{(2)}$	$k_v^{(9)}$	$R_v^{(7)}$	$R_v^{(1)}$	$R_v^{(7)}$	$R_v^{(5)}$
0	28	11	8.4(-24)	0	0	5.9(-14)	0	6.7(-9)
1	20	24	3.9(-17)	1.6(-17)	1.1(-7)	2.7(-7)	2.4(-2)	6.7(-9)
2	14	14	1.2(-14)	8.4(-15)	5.9(-5)	8.4(-5)	4.8(-2)	6.7(-9)
3	10	8	4.2(-13)	3.8(-13)	2.6(-3)	2.9(-3)	7.2(-2)	6.7(-9)
4	7	5	1.4(-12)	1.4(-12)	9.8(-3)	9.8(-3)	9.6(-2)	6.7(-9)
5	0	6	4.8(-12)	4.8(-12)	3.4(-2)	3.4(-2)	1.2(-1)	6.7(-9)

\* Reaction rates (R) are in units of  $\text{cm}^{-3}\text{sec}^{-1}$ , rate constants are in units of  $\text{cm}^3\text{molec}^{-1}\text{sec}^{-1}$ . Numbers enclosed in parentheses are the powers of 10 by which the non-enclosed numbers should be multiplied.

where  $\underline{x}$  is the column vector of  $H_2(v)$  concentrations,  $\underline{R}$  is the column vector of  $H_2(v)$  production rates, and  $K$  is the transition matrix whose elements are given by

$$K_{vv'} = \begin{bmatrix} (k_v^{(2)} + k_v^{(9)}) [0] + k_v^{(7)} [M] + k^{(5)} [O(^1D)] & v' = v \\ k_{v+1}^{(7)} [M] + k_{v+1}^{(9)} [0] & v' = v + 1 \end{bmatrix} \quad (20)$$

Equations 18-20 do not include the effects of transport, which will only be important for  $H_2(v=0)$ . This neglect implies that our calculated values of the concentration of  $H_2(v=0)$  will be too high, but this error will not affect our calculated  $H_2$  destruction rate by processes involving  $H_2^*$ . The calculated values for  $[H_2(v)]$  and the loss rates due to reaction with  $O(^3P)$  are shown in Table 5.

The major result to come from this study is seen at the bottom of Table 5: the total loss rate of  $H_2$  expected due to chemical reactions of  $H_2^*$  with  $O(^3P)$  is approximately  $3.9 \text{ cm}^{-3} \text{ sec}^{-1}$ , compared with a total  $H_2$  production rate (see Table 2) of  $180 \text{ cm}^{-3} \text{ sec}^{-1}$ . Thus, reactions of  $H_2^*$  remove only some 2% of the total  $H_2$  produced at this altitude (80 km). The only other chemical loss process for  $H_2$  important at 80 km is R5, which occurs with a rate of  $5.4 \text{ cm}^{-3} \text{ sec}^{-1}$ . Thus, while  $H_2^*$  makes a substantial contribution to chemical loss of  $H_2$ , the total contribution of chemical losses to the overall  $H_2$  budget is small; most of the  $H_2$  produced at 80 km is transported to higher or lower levels of the atmosphere (Hunten and Strobel, 1974). The very small contribution of loss of  $H_2$  by reaction of  $H_2^*$  to the total  $H_2$  budget suggests that even if we have grossly underestimated  $k_v^{(2)}$ , our conclusion will still be valid.

From Table 2, one may see that 80 km is the most favorable altitude for a contribution of  $H_2^*$  to the overall  $H_2$  chemistry. Away from 80 km,  $H_2$  production is reduced, immediately reducing the potential role of  $H_2^*$  chemistry. Also,  $[O(^1D)]$  is a minimum at 80 km and thus at other altitudes chemical loss of  $H_2$  by R5 will be greater. At lower concentrations the vibrational quenching rates will increase, further limiting the possible contribution of  $H_2^*$ . At higher altitudes the combination of greatly decreased  $H_2$  production and increased  $[O(^1D)]$  will approximately cancel the

Table 5: Contributions of  $H_2^*$  to Loss of  $H_2$  Reaction with  $O(^3P)$  at 80 km\*

v	$k_v^{(2)} (cm^3 molec^{-1} sec^{-1})$	$[H_2(v)] (cm^{-3})$	$R_v^{(2)} (cm^{-3} sec^{-1})$
0	8.4(-24)	8(8) <sup>a</sup>	4.7(-5)
1	3.9(-17)	4.3(3)	1.2(-3)
2	1.2(-14)	1.3(3)	1.1(-1)
3	4.2(-13)	4.3(2)	1.3(0)
4	1.4(-12)	1.5(2)	1.5(0)
<u>5</u>	<u>4.8(-12)</u>	<u>3.2(1)</u>	<u>1.1(0)</u>
sum	---	---	3.9(0)

<sup>a</sup> Numbers in parentheses are the powers of 10 by which the non-enclosed numbers should be multiplied.

<sup>a</sup>  $[H_2(v = 0)]$  is taken from Hunten and Strobel (1974) and not from the results of our calculation, which neglects transport.

increased  $[O(^3P)]$  and decreased total pressure, which would tend to increase the importance of reactions of  $H_2^*$ . Thus, it is apparent that  $H_2^*$  chemistry will not significantly perturb the  $H_2$  budget at any altitude in the mesosphere or lower thermosphere. We emphasize the difference between our results and those of the more complete but less chemically accurate model of Crutzen (1974), who suggested that consideration of R2b might greatly reduce upper atmospheric  $H_2$ . Our differences arise mainly from the different approximations made for the effect of vibrational enhancement on  $k_v^{(2)}$ . The value assumed by Crutzen (1976) for  $v > 1$  is greater than our estimated value for  $v < 5$  at 80 km. Since our model contains a much more realistic chemical treatment for the effect of  $H_2$  vibrational excitation on  $k_v^{(2)}$ , we feel confident that our results more accurately represent the effect of  $H_2^*$  chemistry on atmospheric  $H_2$ .

#### V. Conclusions

We have shown using a realistic chemical model that the contribution of chemical reactions of vibrationally excited  $H_2$  to the total upper atmospheric  $H_2$  budget is negligible. This conclusion differs greatly from the preliminary result of Crutzen (1974) who suggested such a process could lead to a dramatic reduction in upper atmospheric  $H_2$ . Our model contains chemically reasonable values for state-specific reaction rates and branching ratios for the production, chemical reaction, and quenching of  $H_2^*$ . Our estimate that only ~2% of the  $H_2$  produced at 80 km is lost by reaction of  $H_2^*$  is sufficiently small that the conclusion should be independent of the exact assumptions made in our model. Gross errors (i.e. more than an order of magnitude would be necessary to qualitatively alter this conclusion.

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